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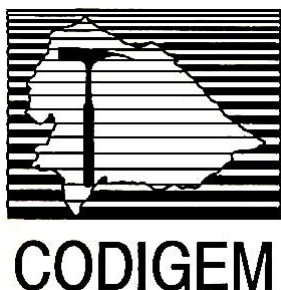
REPORT No. 5

PARTIAL MAP OF THE REPUBLIC OF ECUADOR

**WORLD BANK MINING DEVELOPMENT AND
ENVIRONMENTAL CONTROL PROJECT**

**GEOLOGICAL INFORMATION MAPPING
PROGRAMME
(WESTERN CORDILLERA)**

PATRI MATRIQUE



**MINING DEVELOPMENT AND ENVIRONMENTAL CONTROL
PROJECT**

GEOLOGICAL INFORMATION MAPPING PROGRAMME

Report Number 5

**GEOCHEMICAL ORIENTATION SURVEY, RÍO JUNÍN
SUBCOMPONENT 3.4**

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1. INTRODUCTION

An orientation geochemical survey was undertaken in the Junín area during the period 31 July to 4 August 1995 by Dr. Peter Dunkley, Eng. Johnson Bolaños and Eng. Bolívar Flores.

The objective of the orientation study was to collect a number of different types of fluvial sediment samples to ascertain which would be the best sample medium for the routine geochemical exploration survey of subcomponent 3.4 of the Geological Information Mapping Programme. The samples were subsequently prepared and analysed using a variety of techniques in order to determine which analytical methods would be most suitable and cost effective for the routine survey.

The Junín area was selected for the orientation survey because it is situated within the project area, in the northwest of the Cordillera Occidental, and is the site of a porphyry copper-molybdenum deposit which is known to be associated with a large geochemical anomaly. The area was also considered ideal for an orientation survey because it has no previous history of mining and the geochemical anomaly has therefore neither been complicated nor enhanced by anthropogenic activity.

2. NATURE OF THE JUNÍN PROSPECT

The Junín prospect was discovered in 1981 during the course of a regional geochemical survey undertaken by a Belgian Mission working with INEMIN. Follow-up geological, geochemical and geophysical surveys indicated the presence of a porphyry copper-molybdenum system hosted within granodiorite close to the margin of the Apuela-Nanegal batholith of Miocene age. More recently the prospect has been the subject of an on-going Japanese exploration programme which has drilled a number of boreholes into the main part of the system.

Four alteration zones have been recognised. From the centre to the margins these are a potassic zone, silicic zone, propylitic zone and argillic zone. Both primary (hypogene) and secondary mineralisation (supergene) occur as disseminations and veins. Primary mineral assemblages include pyrite, chalcopyrite, bornite, molybdenite, sulphosalts, haematite (specularite). Tin, tungsten, antimony, arsenic and silver minerals are also reported. Secondary minerals include chalcocite, covellite, cuprite, native copper, chrysocolla and limonite.

A borehole in the most intensely mineralised zone (limonite zone) has proven mineralisation to a depth of more than 150 m (open at depth). Grades range up to 3.84% Cu and average 1.30% Cu over an intersection of 140.8 m which is open at depth. In another mineralised zone (R. Junín mineralised zone) one borehole intersected mineralization between 6.0 m and 233.5 m with grades ranging up to 2.10 % and averaging 0.46%.

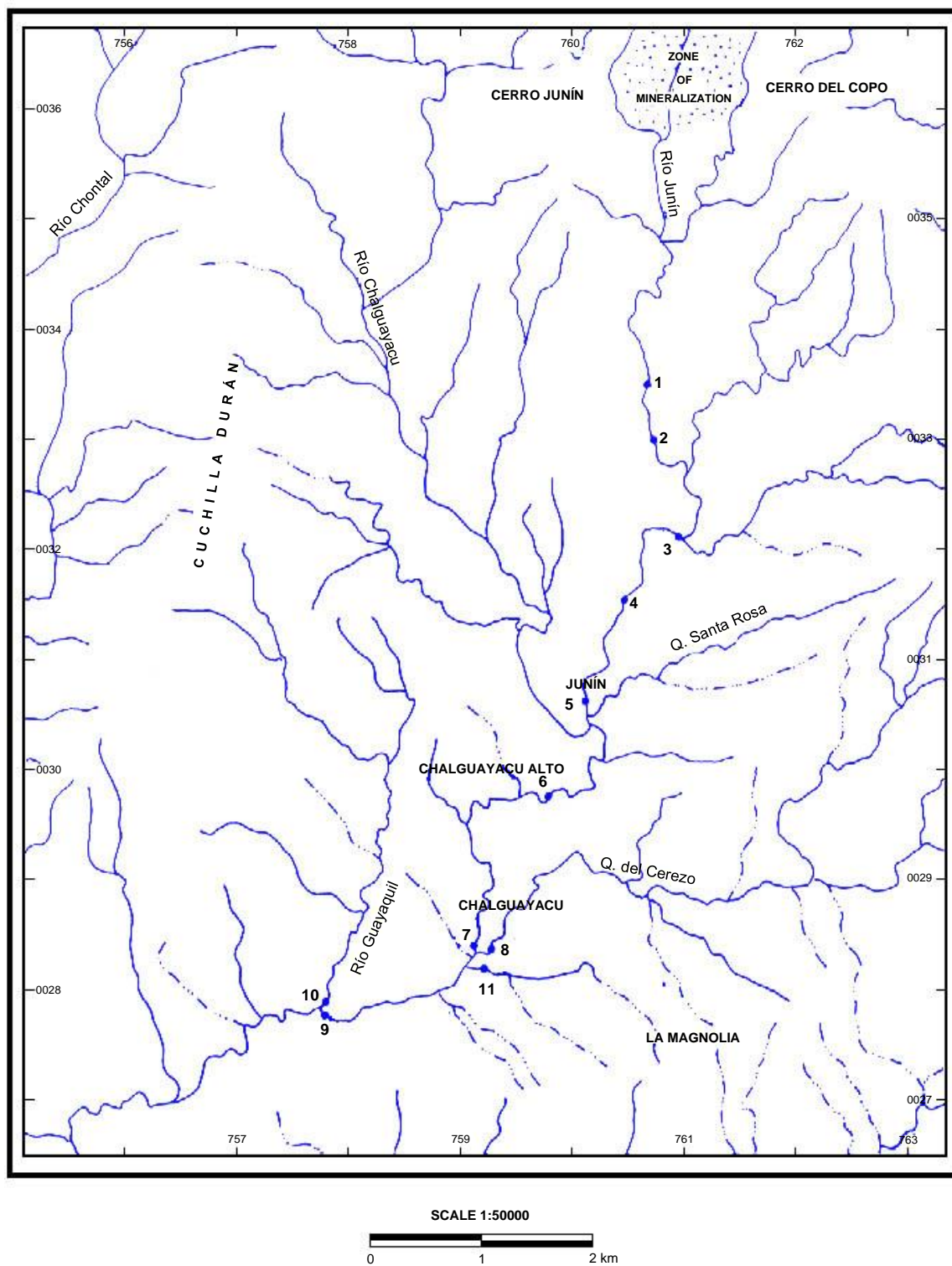


Figure 1. Map of the Junín area showing the location of sample sites

3. SAMPLE COLLECTION AND PREPARATION

3.1 Sample sites

One of the main objectives of the orientation sampling was to ascertain which grain size and which particular elements provide the best means for detecting the mineralisation.

It was originally planned to collect a series of stream sediment samples of different grain sizes along the length of the Río Junín, extending over a distance of 15 km from the most intense mineralisation in the headwaters down to the confluence with the much larger Río Guayllabamba. Unfortunately, the fieldwork coincided with unseasonably wet weather which made the roads impassable. Because of this, only about 80% of the samples could be collected within the time available.

The actual sites that were sampled extend over a distance of about 9 km from the upper reaches of the Río Junín down to its confluence with the Río Guayaquil. This represents a drop in altitude of about 500 metres. Below the confluence with the R. Guayaquil, the Río Junín runs through a gorge for 3 km, where there are no suitable sampling sites. Because of this enforced break in the sampling sequence and also because of the limited time available, it was not considered worth continuing with the sampling in the lowermost reaches of the river where it joins the Guayllabamba.

Three sites were also sampled on tributaries of the Río Junín to provide an approximate measure of background concentrations for comparison with the anomalous values in the main river.

The details of the sample sites are as follows:

Table 1. List of sample sites

No.	Grid Reference	Location
1	760.7-33.6	R. Junín
2	760.7-33.0	R. Junín
3	761.0-32.2	R. Junín
4	760.5-31.6	R. Junín
5	760.2-30.6	R. Junín
6	759.8-29.8	R. Junín
7	759.1-28.4	R. Junín
8	759.2-28.4	Q. del Cerezo
9	757.8-27.8	R. Junín
10	757.8-27.9	R. Guayaquil
11	759.2-28.2	Small tributary draining La Magnolia area

All grid references refer to the 1:50000 topographical map of Vacas Galindo (CT-ÑII-E2).

Site 1 is situated approximately 2 km downstream from the main zone of mineralisation, although large granodiorite boulders show evidence of copper mineralisation at this point. Site 9 is situated about 11 km downstream from the mineralisation.

3.2 Sampling procedure

The river was swiftly flowing. Despite the prolonged and heavy rainfall that coincided with the sampling programme, there was no evidence of flooding and the waters remained clear.

At each sample site active stream sediments were sampled from the drainage channels; at most sites only sediment showing evidence of current ripples was sampled. At all sites the sediment consisted mainly of white to pale grey quartz-feldspathic sands with lesser amounts of amphibole and minor amounts of biotite. Despite the steep terrain and juvenile nature of the river, most sites contained abundant fine sand.

Sediment was collected at each site from a number of different positions within the active stream channel, extending over a stretch of between 10 and 30 metres. Initially sufficient sediment was sieved through a 1 mm nylon sieve to fill a 16-inch diameter plastic prospecting pan with 1 mm sand. The 1 mm fraction was then sieved through a 60 mesh (250 μm) nylon sieve with a gentle rubbing action and the fine fraction collected in a plastic prospecting pan.

As little water as possible (200-300 ml) was used to aid the sieving process. This was contained in a plastic cup and was gradually poured onto the sieve to help separate the fines from the coarser material and wash them through the mesh. The water that was collected in the underlying pan was decanted and recycled through the sieve until all the sieving was completed. In this way fine particles (clays and colloidal oxides) were not lost. When the sieving was completed the sieved sediment and water were left in the prospecting pan for at least 20 minutes to allow suspended fine particles to settle. The supernatant water was then gently poured off, taking as much care as possible to retain the fine material. A small volume of water was left with the sediment and this was agitated and mixed to produce a slurry which was transferred to a Kraft geochemical sample bag through a plastic funnel.

The same process was repeated using a combination of 1 mm and 80 mesh (177 μm) sieves, and 1 mm and 100 mesh (150 μm) sieves to obtain an 80 mesh and a 100 mesh fraction at each site. In all, four size fractions were collected at each site and these were given the following numbers:

Table 2. Size fractions collected

Site	1 mm	60 mesh	80 mesh	100 mesh
1	1/1	1/60	1/80	1/100
2	2/1	2/60	2/80	2/100
3	3/1	3/60	3/80	3/100
4	4/1	4/60	4/80	4/100
5	5/1	5/60	5/80	5/100
6	6/1	6/60	6/80	6/100
7	7/1	7/60	7/80	7/100
8	8/1	8/60	8/80	8/100
9	9/1	9/60	9/80	9/100
10	10/1	10/60	10/80	10/100
11	11/1	11/60	11/80	11/100

3.3 Sample preparation

On their return to Quito the samples were dried in the sun and then prepared for analysis. Dried samples ranged in weight between about 150 grams and 400 grams.

The 1 mm samples were split by riffing and about 75-80 grams milled in an agate laboratory swing-mill (tema) for two minutes. This produced a powder that was finer than about 150-200 microns.

The 60 mesh samples were also split by riffing, and two aliquots of 50-80 grams were crushed in the agate swing-mill. One aliquot was milled for 2 minutes and the other for 1 minute.

The 80 and 100 mesh samples were gently ground by hand using a ceramic mortar and pestle. This was simply to disaggregate the samples which had become caked during the drying process.

The prepared samples were given the following numbers:

Table 3. Prepared samples

Site	1 mm Crushed (2 mins)	60 mesh Crushed (2 mins)	60 mesh Crushed (1 min)	80 mesh	100 mesh
1	1/1	1/60C	1/60	1/80	1/100
2	2/1	2/60C	2/60	2/80	2/100
3	3/1	3/60C	3/60	3/80	3/100
4	4/1	4/60C	4/60	4/80	4/100
5	5/1	5/60C	5/60	5/80	5/100
6	6/1	6/60C	6/60	6/80	6/100
7	7/1	7/60C	7/60	7/80	7/100
8	8/1	8/60C	8/60	8/80	8/100
9	9/1	9/60C	9/60	9/80	9/100
10	10/1	10/60C	10/60	10/80	10/100
11	11/1	11/60C	11/60	11/80	11/100

4. CHEMICAL ANALYSIS

The samples were submitted to Bondar-Clegg Ecuador Ltd. And were forwarded to their laboratories in Vancouver for analysis.

The samples were analysed using the following techniques:

- Aqua regia digestion ($\text{HCl} + \text{HNO}_3$, 3:1), followed by a 34-element package by inductively coupled plasma-atomic emission spectrometry (ICP-AES).
- Multi-acid digestion ($\text{HCl-HNO}_3\text{-HF-HClO}_4$), followed by 34 element package by inductively coupled plasma-atomic emission spectrometry (ICP-AES).
- As and Sb by aqua regia digestion, followed by hydride generation and determination by atomic absorption spectrometry.
- Hg by aqua regia digestion, followed by cold vapour generation and determination by atomic absorption spectrometry.
- Au by fire assay and atomic absorption spectrometry on 20-gram samples.

The purpose of determining the main group of elements by ICP using two different acid attacks was to ascertain which digestion method would give the best anomaly to background contrast. The multi-acid digestion is considered to be a total dissolution method. These two acid digestion methods were used because they are offered as routine techniques by Bondar Clegg. Customized methods of digestion using other acids and fusion techniques were initially considered, but these would have incurred additional costs and would therefore not have been feasible for the routine analytical programme because of budgetary constraints.

5. RESULTS

Although a large number of elements were determined only the analyses of those considered to be of primary importance for detecting mineralisation have been interpreted. These include Cu, Pb, Zn, Mo, As, Sb, Hg and Au.

Graphical plots were prepared showing the variation of concentration for each element with distance downstream from the mineralisation. In the case of Cu, Pb, Zn, Mo and As, which were determined using two acid digestion techniques, two sets of graphs were prepared. The objective of plotting the data in this form was to visually determine which size fractions and which dissolution method give the best anomaly to background contrasts and the greatest anomaly dispersion downstream.

5.1 Copper

The dispersion patterns for copper are clear.

Copper is strongly anomalous for all grain sizes throughout the main drainage. For most grain sizes and both acid digestions, the peak of the anomaly coincides with site 2 (2.75 km downstream), although for the 60 mesh fractions it is slightly higher at site 3 (3.75 km downstream). Although mechanical dispersion probably plays a major role at Junín, the displacement of the copper anomaly peak downstream from the main site of mineralisation could be due to pH variations: At the site of mineralisation pH is probably low, due to oxidizing sulphides at outcrop, whereas a short distance downstream pH is probably higher due to dilution from tributaries, and under these higher pH conditions absorption and coprecipitation of heavy metals may occur.

The following data illustrate a number of significant features of the copper dispersion. All values are given in ppm and background is the average concentration for the three tributaries.

Table 4. Copper by aqua regia-ICP

Mesh fraction	Peak value	Background	Peak/Background
1 mm	854	19.00	44.95
60#	807	19.66	41.05
60C#	802	18.66	41.33
80#	909	20.00	45.45
100#	921	30.00	30.70

Table 5. Copper by HCl-HNO₃-HF-HClO₄-ICP

Mesh fraction	Peak value	Background	Peak/Background
1 mm	972	24.00	40.50
60#	898	27.00	33.20
60C#	889	26.00	34.20
80#	1106	32.00	34.56
100#	1026	38.33	26.77

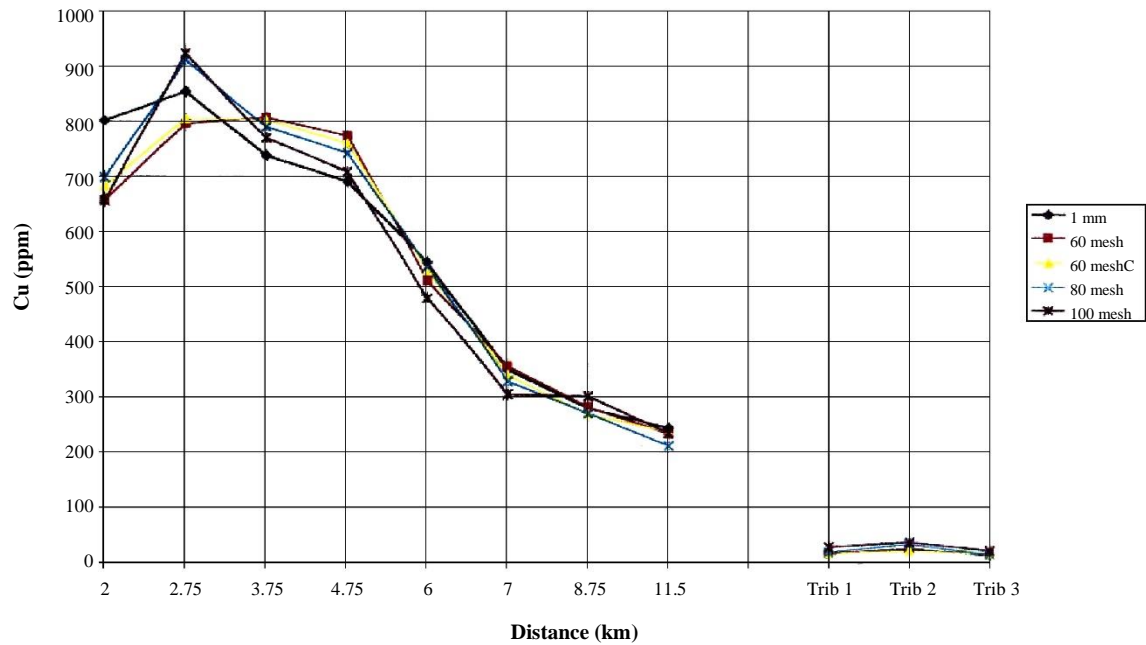


Figure 2. Dispersion pattern for Copper – Aqua Regia digestion

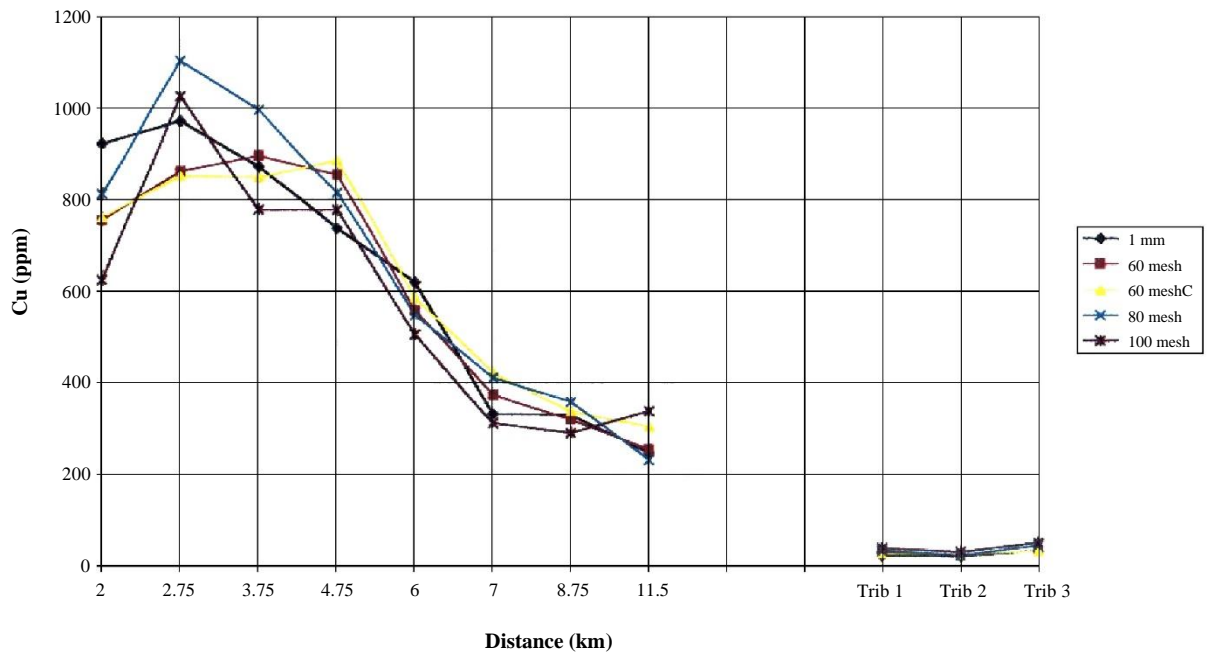


Figure 3. Dispersion pattern for Copper – Total digestion (HCl-HNO₃-HF-HClO₄)

These data indicate that, as might be expected, higher absolute values are obtained by the total acid digestion (HCl-HNO₃-HF-HClO₄) than for the aqua regia digestion. More significant, however, is that for all grain sizes aqua regia digestion produces a better anomaly contrast (peak/background) than the total acid digestion. Furthermore, for both digestions, the 80 mesh fraction gives a much better anomaly/background contrast than the 100 mesh fraction.

5.2 Zinc

All size fractions show relatively weak zinc anomalies in the R. Junín. There also appears to be a zinc anomaly in the tributary Q. del Cerezo (tributary 1 of the graphs). For this reason, the zinc analyses from Q. del Cerezo have not been used in calculating the background, i.e. the background is taken as the average value for the other two tributaries only.

Using the aqua regia digestion, all the size fractions show a broad anomaly in the R. Junín, which is displaced 4 to 6 km downstream from the area of mineralisation, with the anomaly peak occurring at 4.75 km (site 4). As with copper, the total acid digestion gives much higher absolute values but the anomaly contrast (peak/background) is much weaker than for the aqua regia method. For the aqua regia method the anomaly contrast is roughly the same for all grain sizes. Surprisingly, the 1 mm fraction gives the best anomaly contrast, followed closely by the 80 mesh fraction and then by the 100 mesh fraction.

Table 6. Zinc by aqua regia-ICP

Mesh fraction	Peak value	Background	Peak/Background
1 mm	84	43.0	1.95
60#	104	58.5	1.78
60C#	104	56.0	1.86
80#	107	55.5	1.92
100#	117	62.5	1.87

Table 7. Zinc by HCl-HNO₃-HF-HClO₄-ICP

Mesh fraction	Peak value	Background	Peak/Background
1 mm	107	90.5	1.18
60#	131	127.0	1.03
60C#	131	132.5	0.99
80#	149	127.0	1.17
100#	163	132.5	1.23

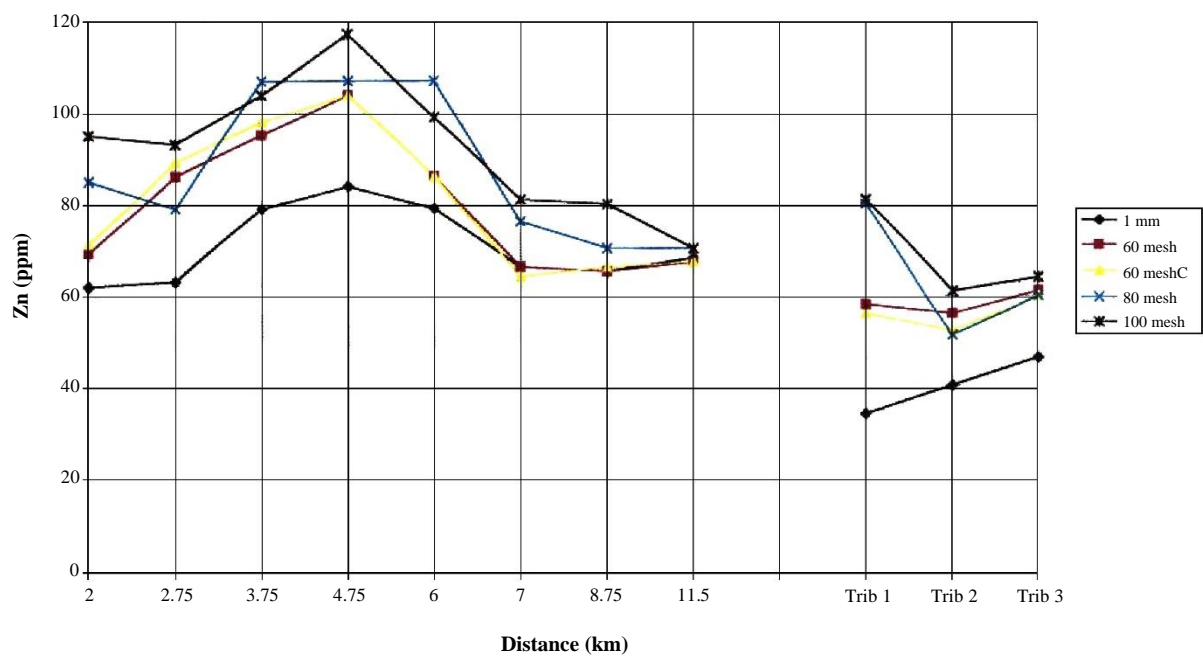


Figure 4. Dispersion pattern for Zinc – Aqua Regia digestion

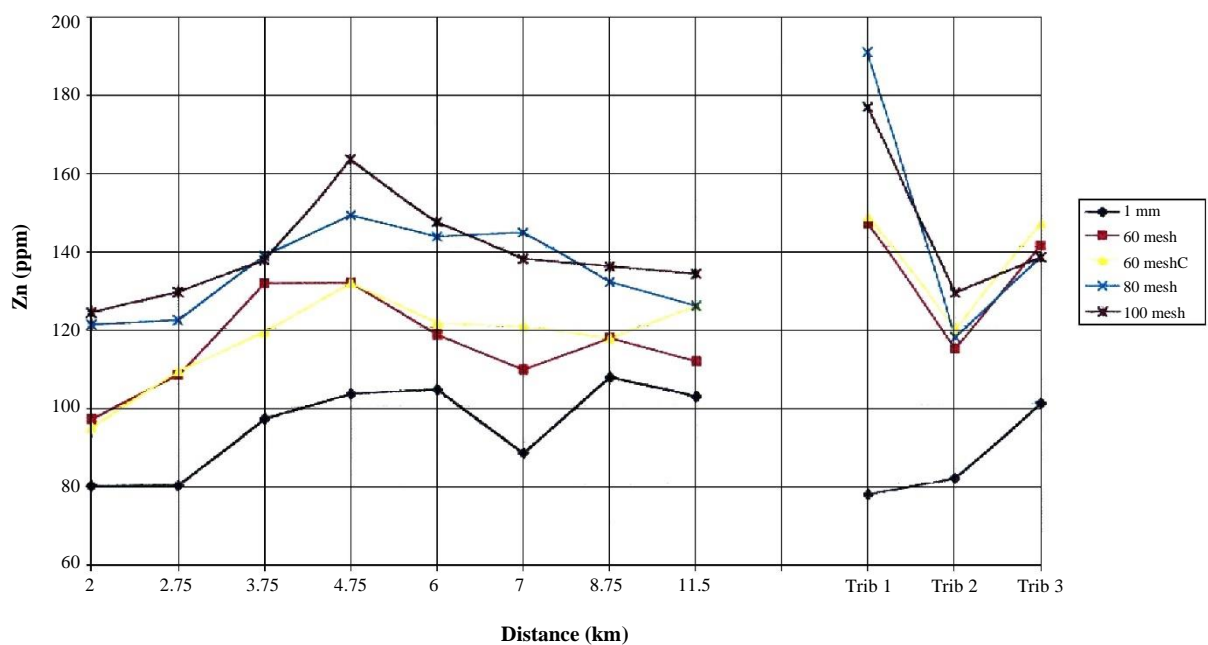


Figure 5. Dispersion pattern for Zinc – Total digestion (HCl-HNO₃-HF-HClO₄)

5.3 Lead

The dispersion patterns for lead are erratic and confusing.

Absolute values are higher using the total acid digestion than for the aqua regia digestion. For the aqua regia digestion many values are close to, or below the detection limit (quoted as 2 ppm Bondar Clegg, but in reality, probably higher). This probably explains the very erratic patterns displayed in the lead graph for aqua regia digestion.

For the total acid digestion, the dispersion patterns are clearer, probably because the values are reasonably well above the detection limit (2 ppm) and precision is therefore better. The dispersion pattern for lead by total acid digestion does not show any obvious anomaly, except that concentrations in the main R. Junín are consistently and significantly higher than in the tributaries. This may not however be related to mineralisation, but may simply reflect the feldspar-rich nature of the sediments derived from the granodiorite in the main river.

Feldspars usually have higher lead contents than other common rock-forming silicates, and with the total acid digestion method this probably gives rise to the higher values in the main river than in the tributaries (which drain relatively feldspar-poor volcanic rocks).

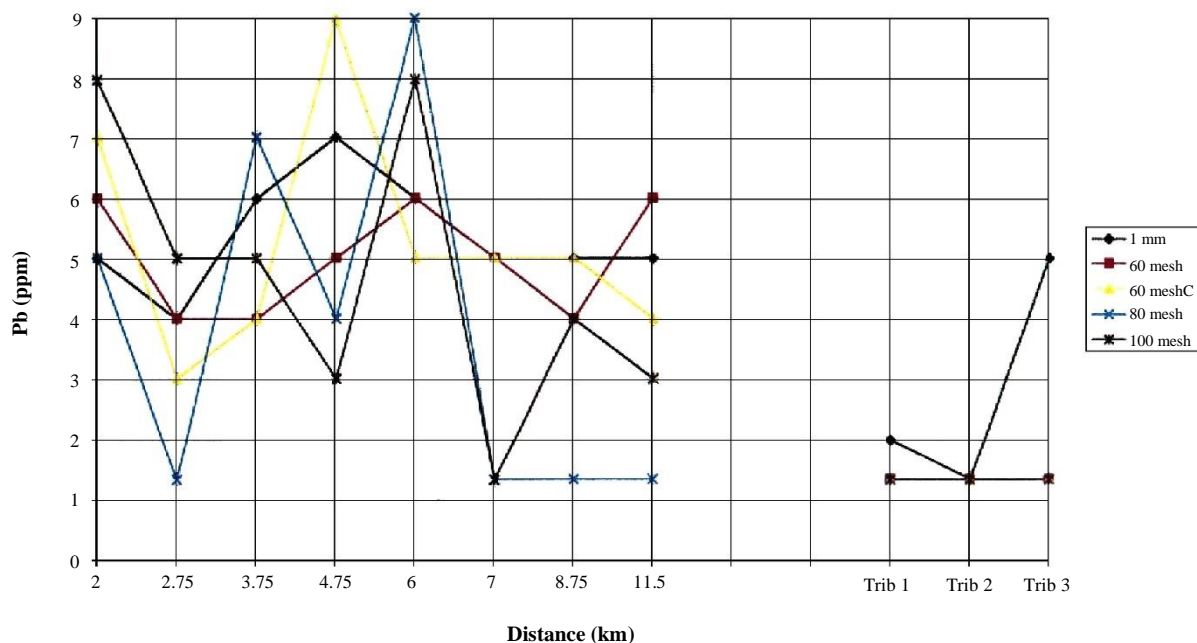
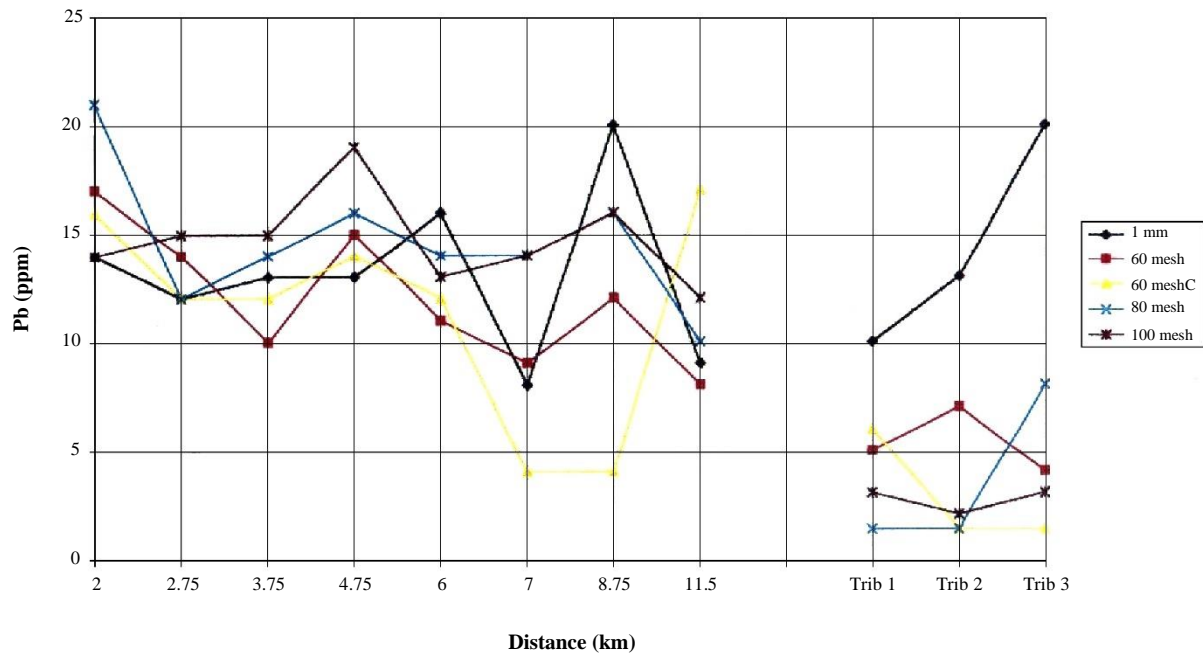


Figure 6. Dispersion pattern for Lead – Aqua Regia digestion


 Figure 7. Dispersion pattern for Lead – Total digestion (HCl-HNO₃-HF-HClO₄)

5.4 Molybdenum

All the size fractions using both digestion techniques show anomalies in molybdenum. As with copper and zinc, the peak of the molybdenum anomaly is displaced downstream (site 2, 2.75 km) from the main zone of mineralisation, and passing farther downstream there is a gradual decay in this anomaly.

Absolute concentrations are generally higher for the total acid digestion method than for aqua regia. For example, values for the peak of the anomaly for the various size fractions range between 14 ppm and 23 ppm using the total digestion method, but only 10 ppm to 14 ppm for the aqua regia digestion. Two reasons may exist for this. Firstly, aqua regia is reported to offer only a partial dissolution technique for molybdenite. The multi-acid attack on the other hand virtually dissolves the sample, liberating metals held within silicate minerals as well as sulphide inclusions within the sediment grains.

The anomaly to background contrast for all the size fractions is better using the aqua regia digestion than the total digestion method. However, for the total digestion method there appear to be anomalies in the finer-sized fractions of Q. del Cerezo, which may bias the background value and hence lower the anomaly/background contrast.

Table 8. Molybdenum by aqua regia-ICP

Mesh fraction	Peak value	Background	Peak/Background
1 mm	10	3.66	2.73
60#	11	6.66	1.65
60C#	11	6.33	1.74
80#	14	6.33	2.21
100#	14	6.00	2.33

Table 9. Molybdenum by HCl-HNO₃-HF-HClO₄-ICP

Mesh fraction	Peak value	Background	Peak/Background
1 mm	14	5.66	2.47
60#	13	11.66	1.11
60C#	13	11.33	1.15
80#	23	14.66	1.57
100#	23	13.00	1.77

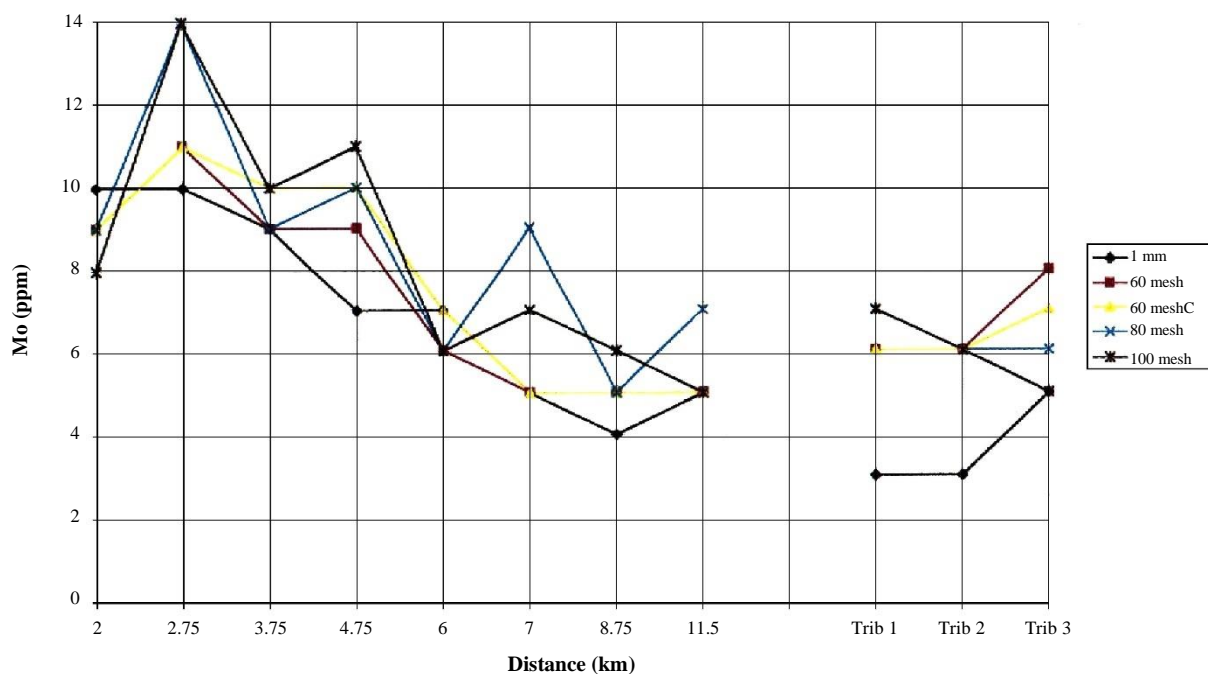
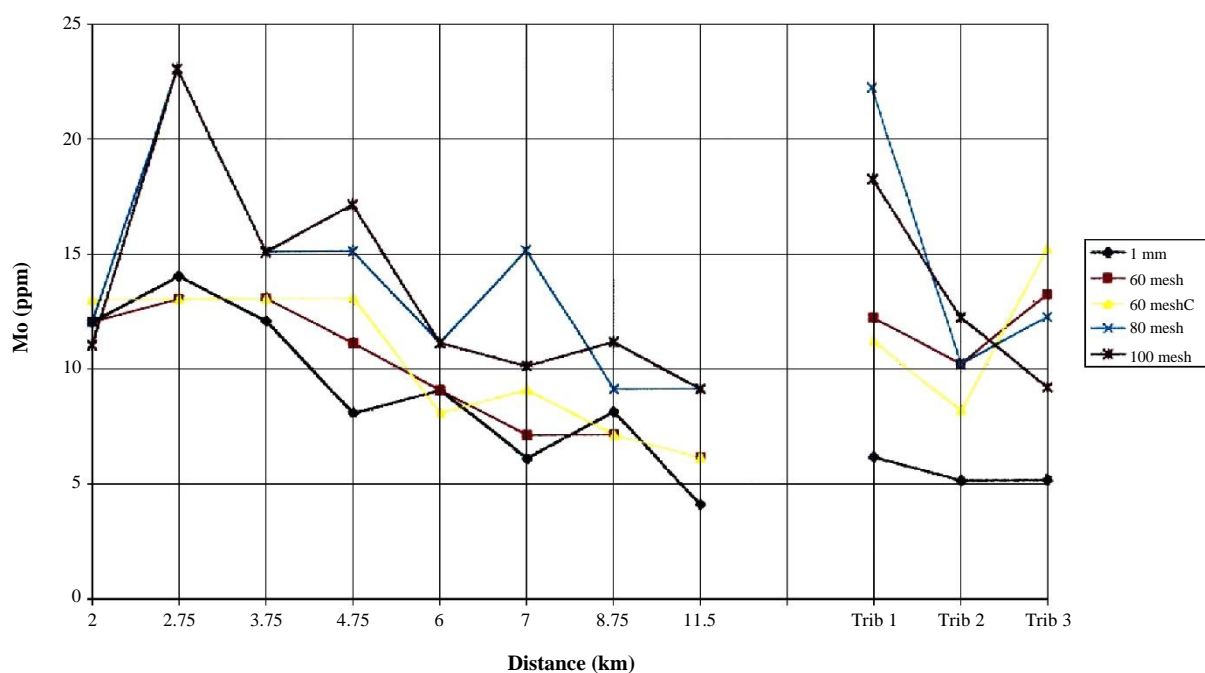


Figure 8. Dispersion pattern for Molybdenum – Aqua Regia digestion

Figure 9. Dispersion pattern for Molybdenum – Total digestion (HCl-HNO₃-HF-HClO₄)

5.5 Arsenic

Arsenic was determined by ICP using both acid dissolution techniques. However, the detection limit reported by Bondar Clegg for As by ICP is 5 ppm, which is considered too high for the requirements of the GIMP geochemical survey. Therefore, As was also determined using the more precise method of aqua regia digestion followed by hydride generation-atomic absorption spectrometry (with a detection limit of 1 ppm according to Bondar Clegg).

Arsenic determined by hydride generation/AAS shows a clear dispersion pattern for all sediment size fractions. As with the other elements, the peak of the anomaly occurs at site 2, approximately 2.75 km downstream from the main zone of mineralisation. Passing farther downstream the anomaly shows a gradual decay. The anomaly/background contrast is greatest for the 80 mesh fraction.

Table 10. Arsenic by aqua regia and hydride generation/AAS

Mesh fraction	Peak value	Background	Peak/Background
1 mm	26.6	5.33	4.99
60#	28.1	2.90	9.69
60C#	28.3	2.70	10.48
80#	33.1	2.83	11.69
100#	31.0	3.46	8.95

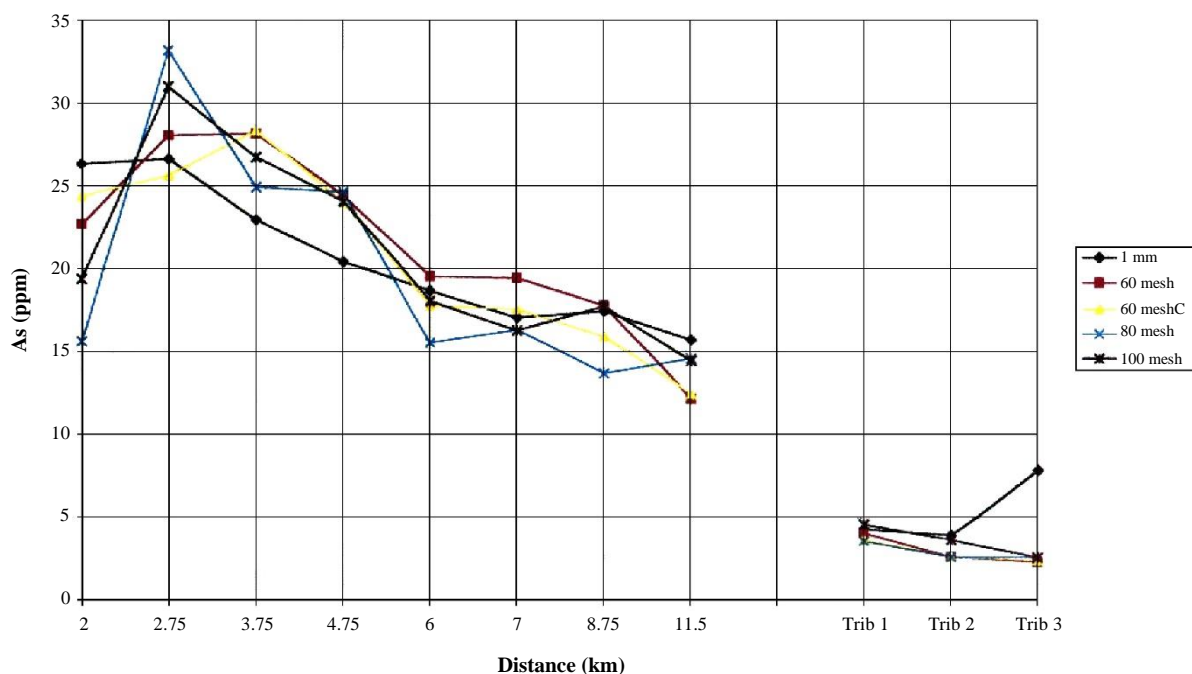


Figure 10. Dispersion pattern for Arsenic – Aqua Regia digestion - Hydride generation - AAS

Arsenic determined by aqua regia digestion and ICP shows similar but much more erratic dispersion patterns, reflecting the lower precision of the method in comparison with the hydride/AAS method. In particular, at several sites the 80 mesh fraction shows values below detection, but by the hydride/AAS method these sites are clearly anomalous. All of the samples taken from the tributaries have As below detection by the aqua regia/ICP method, and it is therefore not possible to assign meaningful background levels nor calculate the anomaly/background contrast for this method.

Arsenic analyses determined by the total digestion technique followed by ICP are highly erratic and fail to illustrate any meaningful dispersion patterns.

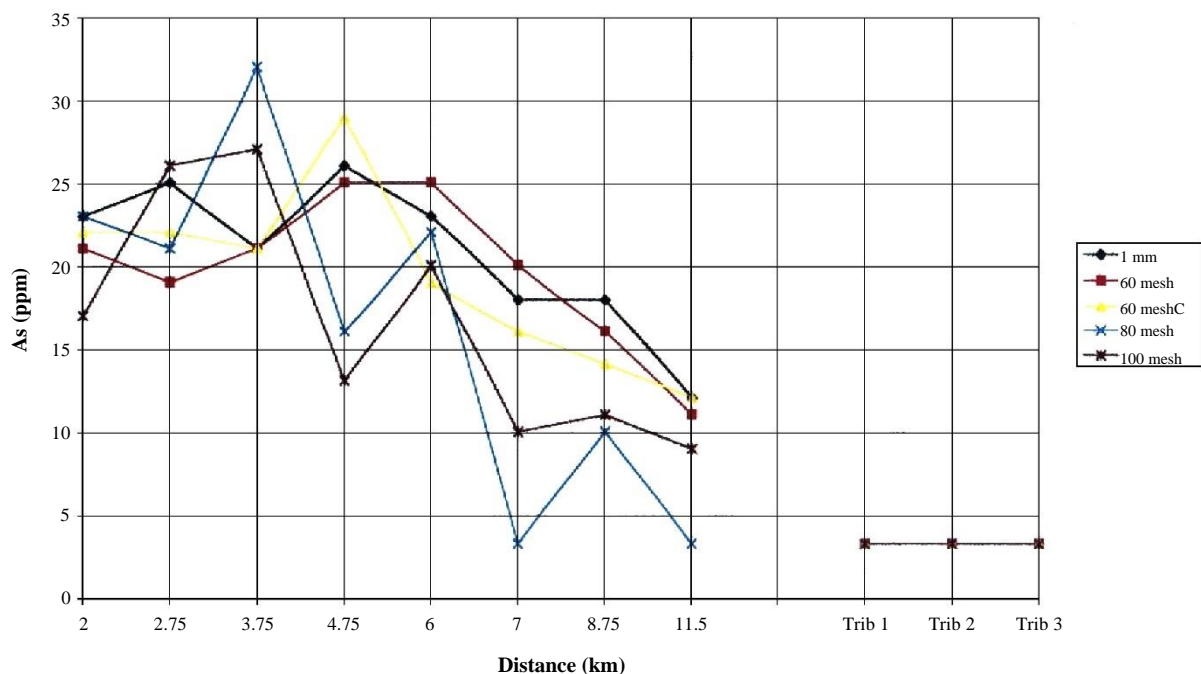


Figure 11. Dispersion pattern for Arsenic – Aqua Regia digestion - ICP

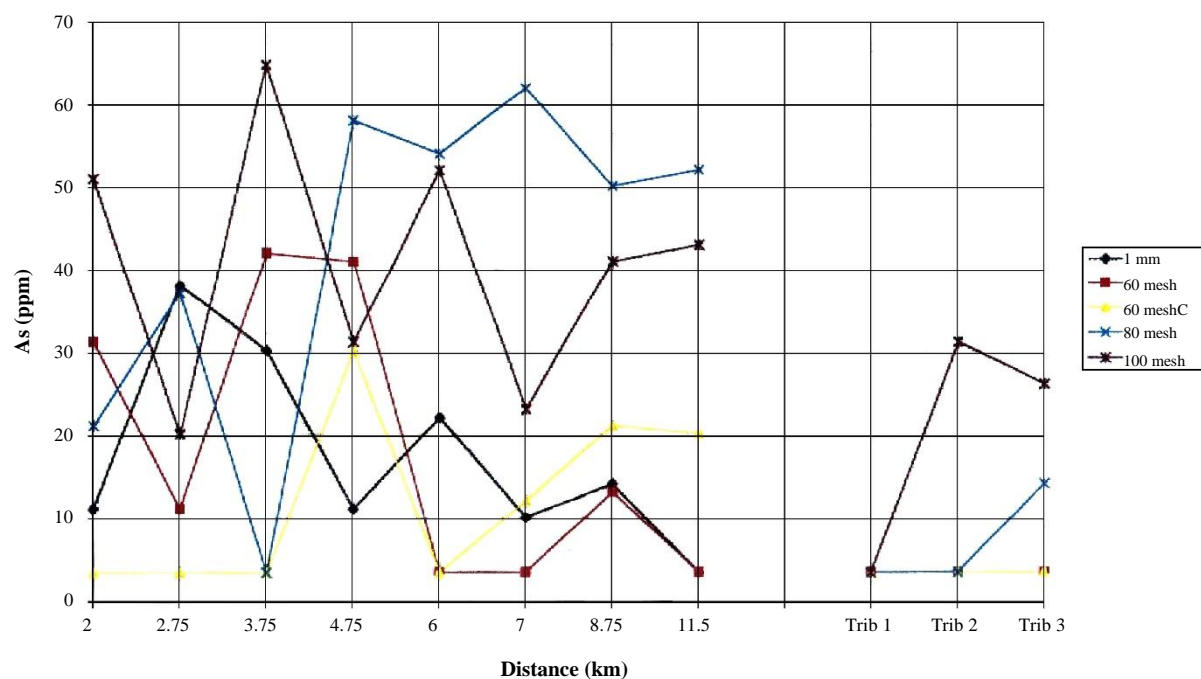


Figure 12. Dispersion pattern for Arsenic – Total digestion (HCl-HNO₃-HF-HClO₄) - ICP

5.6 Antimony

Antimony was determined by ICP using both acid dissolution techniques. However, the detection limit reported by Bondar Clegg for Sb by ICP is 5 ppm, which is considered too imprecise for the requirements of the GIMP geochemical survey. Therefore, Sb was also determined using the more precise method of aqua regia digestion followed by hydride generation-atomic absorption spectrometry (with a detection limit of 0.2 ppm according to Bondar Clegg).

Table 11. Antimony by aqua regia and hydride generation/AAS

Mesh fraction	Peak value	Background	Peak/Background
1 mm	5.4	0.50	10.80
60#	5.1	0.31	16.45
60C#	5.1	0.28	18.20
80#	5.8 (7.9*)	0.40	14.50 (19.75*)
100#	5.7	0.50	11.40

*Second anomaly peak 7 km downstream from main zone of mineralisation

All of the samples in the main river have anomalous Sb when compared with the samples from the three tributaries. The anomaly is slightly displaced downstream from the main zone of mineralisation, although at 7 km the 80 mesh shows a second strong peak. The dispersion train shows a slight decay downstream. Anomaly/background contrasts are higher in the 60 mesh fraction and 80 mesh fractions than in the 100 mesh fraction.

The analysis of antimony by ICP, using both acid dissolution methods, gave results below the detection limit.

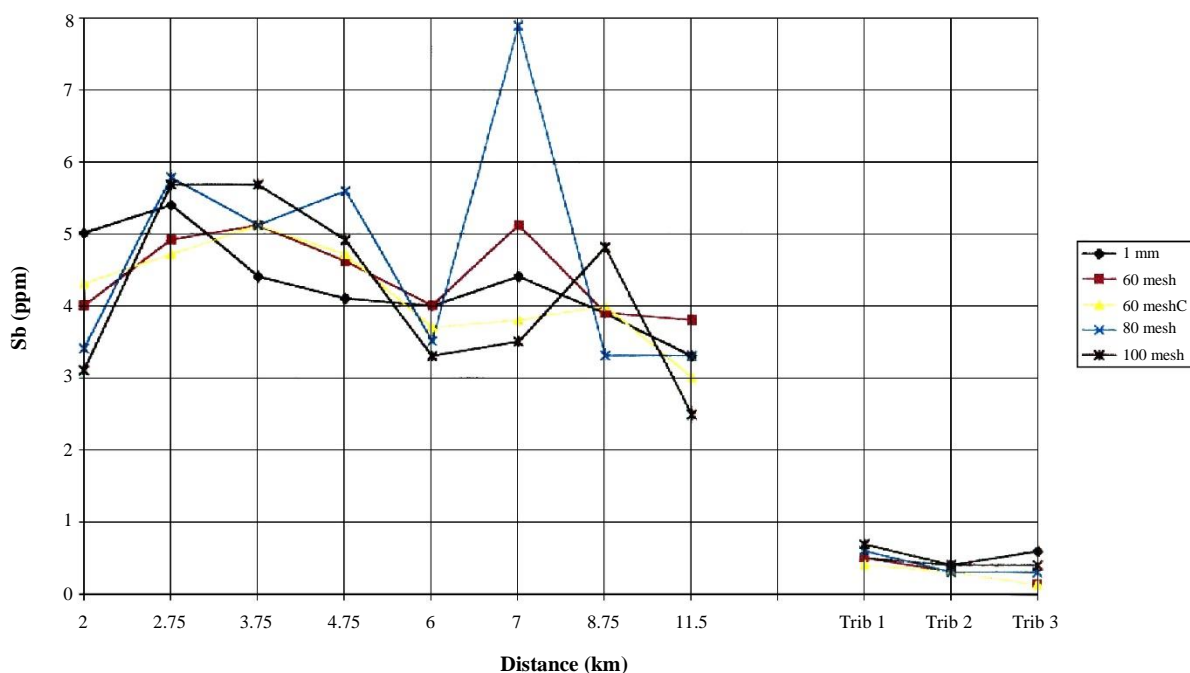


Figure 13. Dispersion pattern for Antimony – Aqua Regia digestion - Hydride generation - AAS

5.7 Mercury

Mercury was analysed by dissolution with aqua regia followed by cold vapour generation and determination by atomic absorption spectrometry. The detection limit of the method according to Bondar Clegg is 0.01 ppm.

Mercury is a useful pathfinder element for the detection of epithermal systems, but it is generally not used for the detection of copper porphyry systems such as Junín. The results however indicate that the sediments in the main R. Junín are consistently, although weakly anomalous when compared with the sediments of the three tributaries.

In the main river Hg values increase slightly downstream in all size fractions. An anomaly peak occurs in the 80 mesh fraction 7 km downstream from the main zone of mineralisation. This could be an erratic analysis because the other size fractions from this site fail to show this anomaly, although the peak of the Sb anomaly also occurs in the 80 mesh fraction at this site.

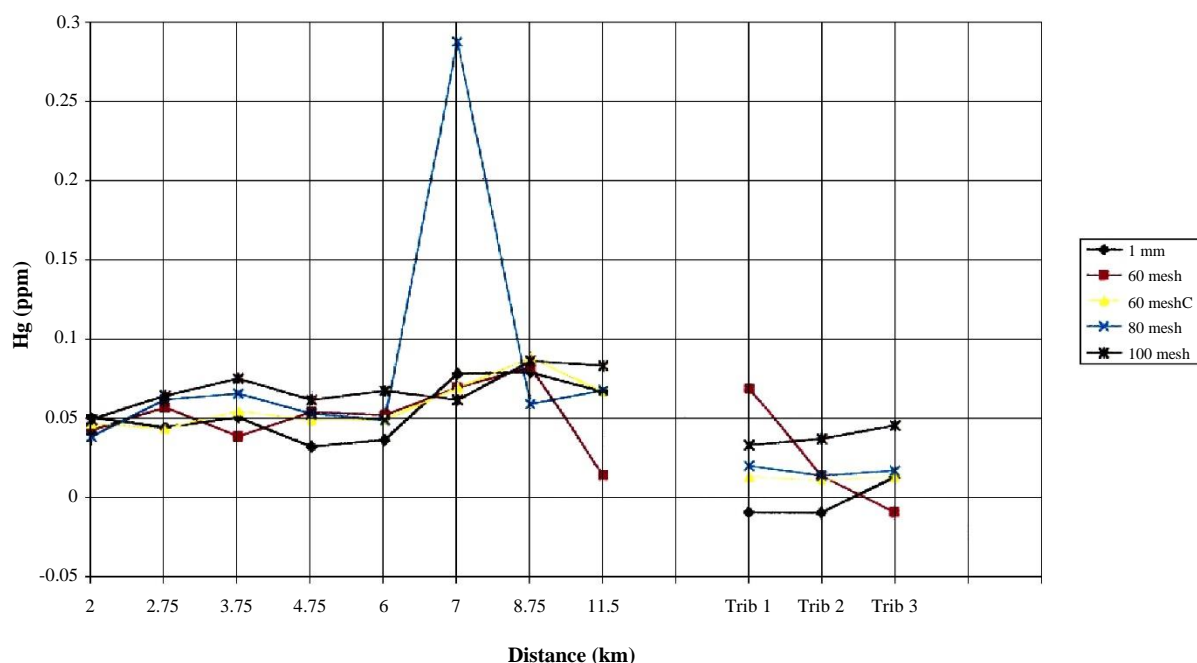


Figure 14. Dispersion pattern for Mercury

5.8 Gold

Gold was determined by a combined fire assay and atomic absorption spectrometry on 20-gram aliquots of sediment. The detection limit of the method is reported by Bondar Clegg to be 5 ppb. Conventionally 30-gram samples are normally analysed by fire assay. Although this provides a more representative sample, it was felt that it might not be possible to obtain sufficient fine sediment at many sites for a 30-gram assay, bearing in mind the need to duplicate some analyses and also archive sufficient sample. For this reason, a 20-gram aliquot was chosen.

Anomalous gold values occur within the drainage basin. However, many of the analyses gave results below the detection limit, thus making it impossible to calculate meaningful background values and anomaly/background contrast.

The distribution patterns for gold indicate that for most of the grain sizes concentrations are close to, or below the detection limit. However, for the 100 mesh fraction there are several clear anomalies and all but one site gave values above the detection limit. The Guayaquil tributary shows a strong anomaly in the 1 mm fraction and a small anomaly in the 100 mesh fraction.

Due to the sampling difficulties inherent in geochemical exploration for gold it is difficult to draw firm conclusions from the limited data obtained from the Junín orientation survey. Furthermore, the Junín prospect is not particularly anomalous in gold and is therefore not a good choice for such an orientation survey specifically for this element. However, from the limited data available, it appears that the finer-sized fractions produced more analyses above the detection limit than the coarser fractions. In particular the 100 mesh fraction produced the most consistent results, showing a weak but broad anomaly dispersed over several sites within the main river.

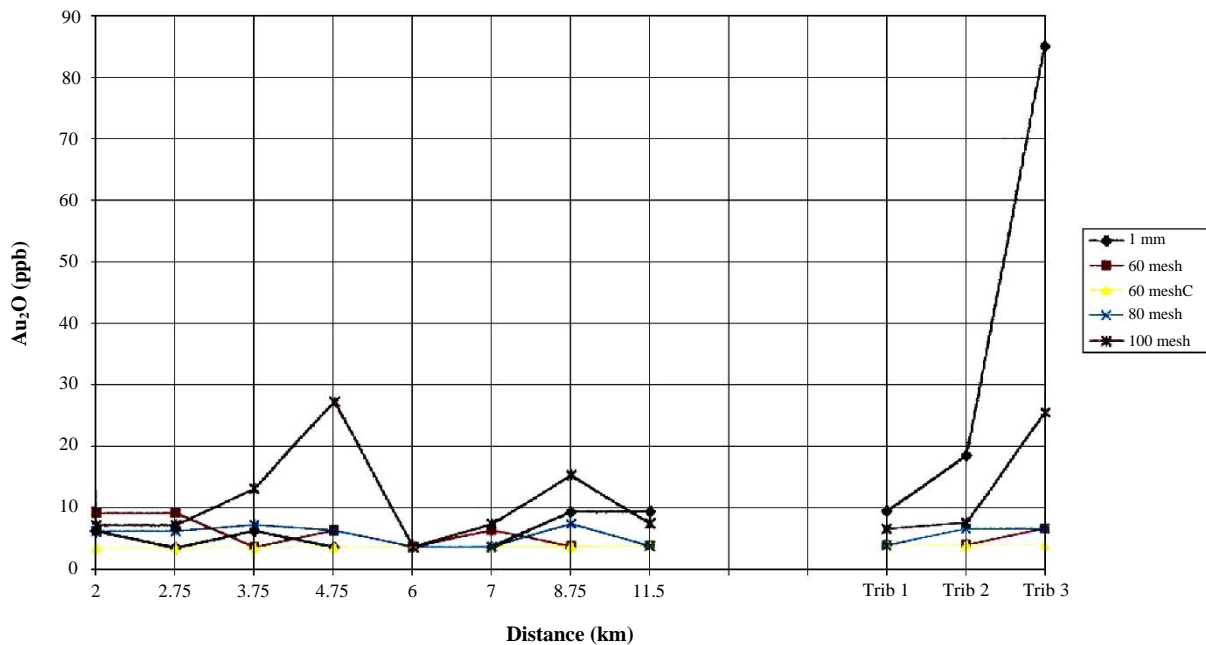


Figure 15. Dispersion pattern for Gold

6. DISCUSSION AND CONCLUSIONS

Given the large variations in altitude, climate, vegetation and geology within the Cordillera Occidental, caution must be exercised in designing a general working method for the geochemical exploration of the entire cordillera based upon the results of a single orientation survey over a specific mineral deposit. Different deposit types have different geochemical signatures, which are further complicated by surficial processes which vary with terrain and climate. For example, the surface geochemical signature of a precious metal epithermal deposit in an area of páramo will not be the same as that of a Cu-Mo porphyry deposit within the rain forest of the western foothills, such as that at Junín.

Ideally, several orientation surveys should be undertaken over a number of different deposit types in various climatic settings, but at the beginning of the GIMP time was not available for such an approach. However, had such an approach been applied, it would probably not have been possible to reconcile the optimum techniques for detecting each type of mineralisation under differing climatic settings within a single working method. In a regional geochemical survey of a strategic nature, such as that of the GIMP, a relatively simple and robust methodology needs to be applied throughout the life of the survey. This must not be biased towards exploration for any single type of mineral deposit, and it should also be kept in mind that the results of the survey have utility not only for mineral exploration but also with respect to environmental issues and resource management in general.

The Junín deposit is large and is being actively eroded, and is associated with a pronounced geochemical anomaly which extends for at least 11 km downstream. The fact that the anomaly for certain elements is strong within the 1 mm fraction as well as the finer fractions suggests an important mechanical component in the dispersion of the anomaly.

In general, finer sediment fractions give the best anomaly to background contrast and longest dispersion trains and are normally used in geochemical exploration. Although a good anomaly/background contrast occurs for certain elements at Junín within the coarse fraction as well as the finer fractions, this should be viewed as an exception, and is very unlikely to be the case for most of the other zones of mineralisation within the cordillera. For Au and the important pathfinder elements As and Sb, however, the finer fractions at Junín give a much better response than the coarser fractions. Selection of a suitable grain size for the routine sampling programme should therefore be confined to the finer fractions.

For the base metals, Cu and Zn, the 80 mesh fraction gives better background/anomaly contrasts than the 60 mesh and 100 mesh fractions, except for Zn by HCl-HNO₃-HF-HClO₄ which is slightly better in the 100 mesh fraction than 80 mesh fraction. For Mo on the other hand a slightly better anomaly/background contrast was obtained with the 100 mesh fraction than with the 80 mesh fraction and a considerably better contrast than with the 60 mesh fraction. For all three elements (Cu, Zn and Mo) the aqua regia digestion produces lower absolute concentrations but gives far better anomaly/background contrasts than the HCl-HNO₃-HF-HClO₄ digestion.

For the pathfinder elements As and Sb, the precision of analyses by the ICP method is poor and the detection limits, quoted as 5 ppm for both elements but in reality probably greater, are too high for the requirements of the survey. The ICP analyses for As using aqua regia digestion are erratic, but do show the anomaly, whereas those using the HCl-HNO₃-HF-HClO₄ digestion show extremely erratic results and do not highlight the anomaly. All of the Sb analyses by ICP were below the detection limit. Analyses of these two elements by aqua regia digestion followed by hydride generation and determination by AAS produce much more precise data and clearly detect the anomaly in the main river. The highest concentrations and the greatest anomaly/background contrast for As occur in the 80 mesh fraction, and the 60 mesh fraction also gives a greater contrast than the 100 mesh fraction. A similar pattern is seen for Sb, with the 80 mesh giving a better response than the 100 mesh once again.

The Junín prospect is only very weakly anomalous with respect to Au and is therefore not a good location for an orientation survey specifically for this element. However, the 100 mesh fraction does detect a broad but weak anomaly within the main river.

In conclusion, it would appear that the 80 mesh fraction produces better anomaly/background contrasts than the 100 mesh fraction for the majority of the elements, and considerably better contrasts than the 60 mesh fraction for all the elements.

Another factor which needs to be taken into account when selecting the optimum sample size fraction for the routine survey, is that many of the rivers within the region are highly energetic and therefore contain little fine sediment. As a result, at many sites it is difficult and time consuming, and at times impossible to collect sufficient fine material: With regard to this problem, it is interesting to note that previous regional geochemical surveys by British and Belgian missions in Ecuador sampled the 60 mesh fraction, and that the Belgian mission later changed to sampling the 1 mm fraction because it was considered too time consuming to sieve to 60 mesh. This is not ideal, because general experience and the results of the present orientation survey indicate that the 60 mesh fraction does not give a particularly good geochemical anomaly response. Furthermore, although it is difficult and in places impossible to obtain fine sediment in the rivers in the higher parts of the cordillera, it is usually possible to sieve sufficient 80 mesh material (but not 100 mesh) within a reasonable time (e.g. 40 minutes to 1 hour per sample).

Taking into account the results of the Junín orientation survey, and also the general lack of very fine sediment in the rivers of the cordillera, it is concluded that on balance the 80 mesh size fraction, rather than the 100 mesh fraction, offers the best sampling medium for the routine geochemical survey.

Of the two acid digestion methods applied during the orientation survey, aqua regia consistently produced the best anomaly/background contrasts for all of the elements of interest and is therefore the best option for the routine geochemical survey.

The analysis of the pathfinder elements As and Sb in the main 34-element package by ICP is too imprecise for the purpose of the survey, especially using the HCl-HNO₃-HF-HClO₄ digestion which gives extremely erratic results. In contrast the precision of analyses obtained for As and Sb by aqua regia digestion, followed by hydride generation and AAS determination appears to be good. This method is therefore recommended for the routine survey. It has the added advantage that, these two elements can be determined on the same (aqua regia solution) as the main group of elements by ICP, so keeping the cost of the overall analytical package to a minimum.

7. RECOMMENDATIONS FOR THE ROUTINE SURVEY

i. The 80 mesh size fraction is recommended as the best all-round sampling medium for the purpose of the routine survey. A description of the sampling method is given in the Appendix 2 at the end of this report.

ii. The following analytical scheme is recommended for the routine survey:

- Aqua regia digestion ($\text{HCl} + \text{HNO}_3$, 3:1) followed by:

34 element package by inductively coupled plasma-atomic emission spectrometry.

As and Sb in the same solution by hydride generation and determination by atomic absorption spectrometry.

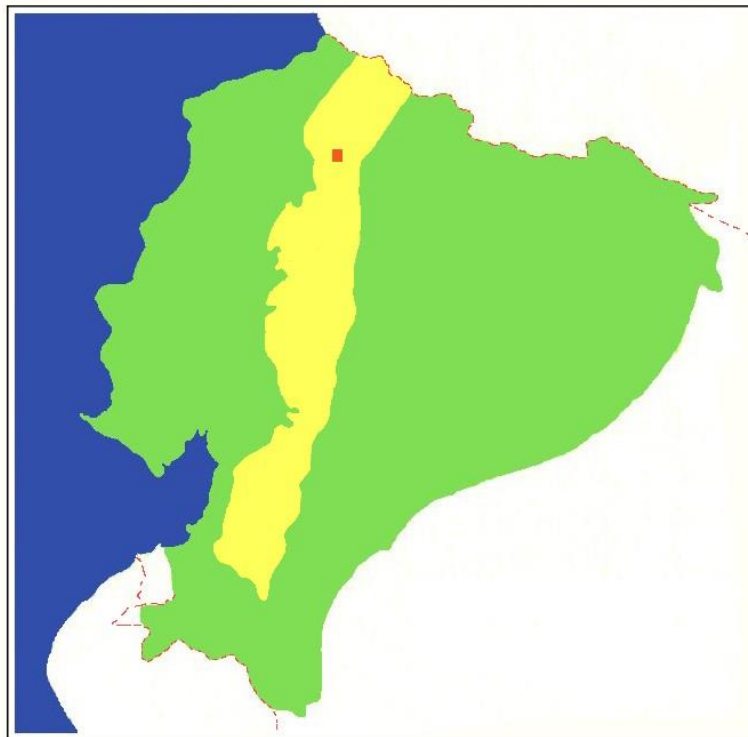
Hg in the same solution by cold vapour generation and determination by atomic absorption spectrometry.

- Au by fire assay and atomic absorption spectrometry on 20-gram samples.

APPENDIX 1 OF REPORT:

GEOCHEMICAL ORIENTATION SURVEY, RÍO JUNÍN

STREAM SEDIMENT ANALYSES



GEOLOGICAL INFORMATION MAPPING PROGRAMME

QUITO, 1997

RESULTS OF CHEMICAL ANALYSES

Table 1. Analyses of stream sediments. Analyses by aqua regia digestion-ICP (ppm).

Negative values indicate below detection limit

Sample	Cu tot	Pb tot	Zn tot	Mo tot	As tot
1/1	924	14	80	12	11
2/1	972	12	80	14	38
3/1	875	13	97	12	30
4/1	734	13	103	8	11
5/1	618	16	104	9	22
6/1	332	8	88	6	10
7/1	329	20	107	8	14
8/1	21	10	77	6	-5
9/1	246	9	102	4	-5
10/1	19	13	81	5	-5
11/1	32	20	100	5	-5
1/60	752	17	97	12	31
2/60	864	14	108	13	11
3/60	898	10	131	13	42
4/60	856	15	131	11	41
5/60	556	11	118	9	-5
6/60	374	9	109	7	-5
7/60	319	12	117	7	13
8/60	28	5	146	12	-5
9/60	253	8	111	6	-5
10/60	21	7	114	10	-5
11/60	32	4	140	13	-5
1/60C	758	16	95	13	-5
2/60C	854	12	109	13	-5
3/60C	850	12	119	13	-5
4/60C	889	14	131	13	30
5/60C	584	12	121	8	-5
6/60C	421	4	120	9	12
7/60C	337	4	117	7	21
8/60C	25	6	148	11	-5
9/60C	303	17	125	6	20
10/60C	22	-2	119	8	-5
11/60C	31	-2	146	15	-5
1/80	812	21	121	12	21
2/80	1106	12	122	23	37
3/80	996	14	138	15	-5
4/80	814	16	149	15	58
5/80	546	14	143	11	54
6/80	410	14	144	15	62
7/80	359	16	131	9	50
8/80	32	-2	190	22	-5
9/80	230	10	125	9	52
10/80	21	-2	117	10	-5
11/80	43	8	137	12	14
1/100	623	14	124	11	51
2/100	1026	15	129	23	20
3/100	776	15	137	15	65
4/100	775	19	163	17	31
5/100	503	13	147	11	52
6/100	311	14	137	10	23
7/100	289	16	135	11	41
8/100	37	3	176	18	-5
9/100	338	12	133	9	43
10/100	28	2	128	12	31
11/100	50	3	137	9	26

Table 2. Analyses of stream sediments. Au by fire assay-AAS (ppb).

Negative values indicate below detection limit

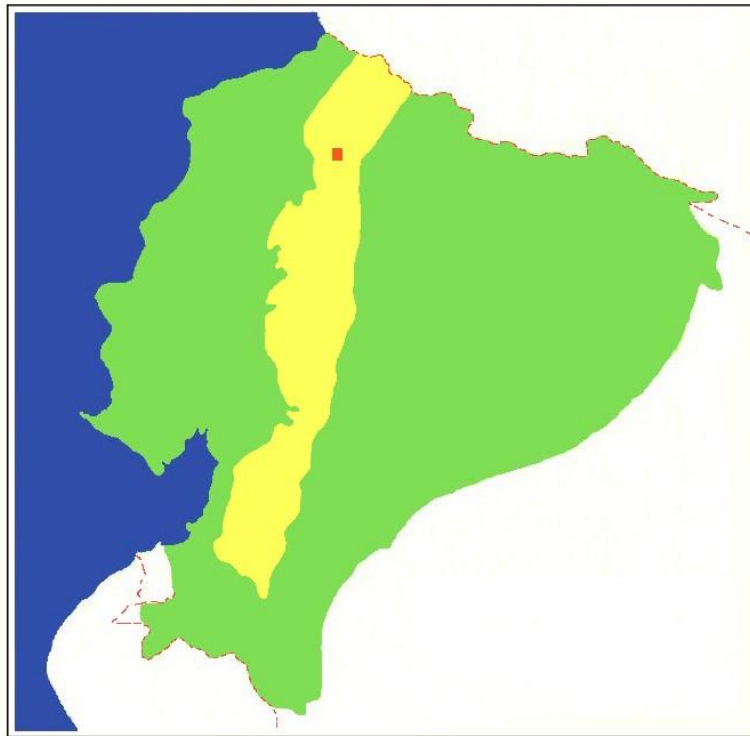
Sample	Au	Cu ar	Pb ar	Zn ar	Mo ar	As ar	Sb ar	As hyd	Sb hyd	Hg
1/1	6	801	5	62	10	23	-5	26.3	5	0.05
2/1	-5	854	4	63	10	25	-5	26.6	5.4	0.044
3/1	6	736	6	79	9	21	-5	23	4.4	0.05
4/1	-5	690	7	84	7	26	-5	20.4	4.1	0.032
5/1	-5	542	6	79	7	23	-5	18.7	4	0.036
6/1	-5	346	5	66	5	18	-5	17.1	4.4	0.078
7/1	9	279	5	65	4	18	-5	17.5	3.9	0.079
8/1	9	16	2	34	3	-5	-5	4.3	0.5	-0.01
9/1	9	244	5	68	5	12	-5	15.7	3.3	0.066
10/1	18	15	-2	40	3	-5	-5	3.9	0.4	-0.01
11/1	85	26	5	46	5	-5	-5	7.8	0.6	0.013
1/60	9	656	6	69	9	21	-5	22.7	4	0.042
2/60	9	794	4	86	11	19	-5	28	4.9	0.056
3/60	-5	807	4	95	9	21	-5	28.1	5.1	0.038
4/60	6	772	5	104	9	25	-5	24.4	4.6	0.053
5/60	-5	510	6	86	6	25	-5	19.5	4	0.051
6/60	6	352	5	66	5	20	-5	19.4	5.1	0.069
7/60	-5	281	4	65	5	16	-5	17.8	3.9	0.082
8/60	-5	18	-2	58	6	-5	-5	4	0.5	0.014
9/60	-5	233	6	67	5	11	-5	12.1	3.8	0.068
10/60	-5	17	-2	56	6	-5	-5	2.5	0.3	0.014
11/60	6	24	-2	61	8	-5	-5	2.2	-0.2	-0.01
1/60C	-5	681	7	71	9	22	-5	24.4	4.3	0.046
2/60C	-5	804	3	89	11	22	-5	25.6	4.7	0.043
3/60C	-5	802	4	98	10	21	-5	28.3	5.1	0.054
4/60C	-5	758	9	104	10	29	-5	24	4.7	0.048
5/60C	-5	528	5	86	7	19	-5	17.8	3.7	0.048
6/60C	-5	337	5	64	5	16	-5	17.6	3.8	0.069
7/60C	-5	269	5	66	5	14	-5	15.9	4	0.088
8/60C	-5	17	-2	56	6	-5	-5	3.6	0.4	0.013
9/60C	-5	236	4	67	5	12	-5	12.4	3	0.066
10/60C	-5	17	-2	52	6	-5	-5	2.5	0.3	0.011
11/60C	-5	22	-2	60	7	-5	-5	2.3	-0.2	0.013
1/80	6	697	5	85	9	23	-5	15.6	3.4	0.038
2/80	6	909	-2	79	14	21	-5	33.1	5.8	0.061
3/80	7	789	7	107	9	32	-5	24.9	5.1	0.065
4/80	6	740	4	107	10	16	-5	24.6	5.6	0.052
5/80	-5	535	9	107	6	22	-5	15.5	3.5	0.048
6/80	-5	326	-2	76	9	-5	-5	16.3	7.9	0.287
7/80	7	270	-2	70	5	10	-5	13.6	3.3	0.058
8/80	-5	20	-2	80	7	-5	-5	3.5	0.6	0.02
9/80	-5	211	-2	70	7	-5	-5	14.5	3.3	0.067
10/80	6	16	-2	51	6	-5	-5	2.5	0.3	0.014
11/80	6	34	-2	60	6	-5	-5	2.5	0.3	0.017
1/100	7	655	8	95	8	17	-5	19.4	3.1	0.049
2/100	7	921	5	93	14	26	-5	31	5.7	0.064
3/100	13	768	5	104	10	27	-5	26.7	5.7	0.075
4/100	27	707	3	117	11	13	-5	24.1	4.9	0.061
5/100	-5	479	8	99	6	20	-5	18.1	3.3	0.067
6/100	7	303	-2	81	7	10	-5	16.3	3.5	0.061
7/100	15	300	4	80	6	11	-5	17.8	4.8	0.086
8/100	6	29	-2	81	7	-5	-5	4.6	0.7	0.033
9/100	7	235	3	70	5	9	-5	14.4	2.5	0.083
10/100	7	23	-2	61	6	-5	-5	3.6	0.4	0.037
11/100	25	38	-2	64	5	-5	-5	2.5	0.4	0.045

ar = aqua regia followed by ICP (ppm); hyd = aqua regia digestion followed by hydride generation and AAS (ppm)

APPENDIX 2 OF REPORT:

GEOCHEMICAL ORIENTATION SURVEY, RÍO JUNÍN

SAMPLING METHOD



GEOLOGICAL INFORMATION MAPPING PROGRAMME

QUITO, 1997

COLLECTION OF STREAM SEDIMENT SAMPLES FOR GEOCHEMICAL ANALYSIS

Site selection

The site should be located as close as possible to that pre-selected on the 1:50000-scale topographic map.

Every attempt should be made to collect the sample from the active drainage channel. Bank-slip material should be avoided. Wherever possible sandy areas should be sampled in preference to gravels and a composite sample should be collected by taking material from a number of locations over distances of a few tens of metres (up to 50 metres if necessary) along the active drainage channel.

Obvious contamination should be avoided. For example, where roadside sites are to be sampled the sample should be collected upstream from bridging points.

Procedure

N.B. Before commencing all hand jewellery should be removed and rubber gloves should be worn:

1. Using the trenching tool, collect sufficient active stream sediment in the plastic prospecting pan. The surface oxidised sediment should first be removed and the sediment collected from a depth of 10-30 cm. Take care to remove any coarse pebbles or cobbles and use the minimum amount of water when loading the pan.
2. Place the 2 mm sieve (16-inch diameter wooden sieve with nylon mesh) over a plastic prospecting pan and carefully shake and rub (by hand) the sediment through the mesh. Use a small amount of water poured sparingly from a plastic cup to help separate and wash the fine material through the sieve. Do not use more than a cupful of water (about 250 ml). As and when necessary, the water may need to be decanted from the prospecting pan into the cup and recycled through the sieve. The purpose of recycling is to use as little water as possible so that fine particles (clays and colloidal oxides, etc.) are not lost from the sample. Avoid overloading the sieve and from time to time discard the coarse material and reload with fresh sediment, repeating the process until sufficient 2 mm sediment has been collected (always recycling the same water).
3. When sufficient 2 mm material is judged to have been collected this should be sieved through the 80 mesh (177 μ m) sieve fixed over a clean plastic prospecting pan. Do not overload the sieve. Gently rub small portions of the 2 mm sediment through the 80 mesh sieve, shaking from time to time and using the recycled water retained from Step 2 to help separate and wash the fines through the mesh. From time to time discard the oversize material and reload with fresh 2 mm sediment. Decant and recycle the same water as and when necessary.

4. When sufficient 80 mesh material has been collected, leave the prospecting pan together with the fine sediment fraction and supernatant water for 15 minutes or more, to allow as much of the finer suspended sediment to settle. During this 'rest period' a sample registration form may be completed and a heavy mineral concentrate collected.
5. After a minimum of 15 minutes, slowly and carefully decant off most of the water, leaving a small amount in the pan with the sediment sample. Avoid discarding fine material which has obviously settled out of suspension. Homogenize the remaining water with the sediment by gently agitating to produce a slurry.
6. Take a plastic funnel (thoroughly cleaned with river water) and use this to carefully transfer the sediment-water mixture to a prenumbered Kraft sample bag. Seal the sample bag and place within a polythene bag and tie a loose knot.
7. Place the sample in a plastic box to prevent damage and cross-contamination during transport. Place the box in a rucksack taking care that the sample remains upright.
8. All equipment should be washed in river water before moving on to the next site.
9. At the end of each day, or when the samplers return to the field base, the samples should be removed from the plastic bags. If there has been significant leakage of sediment, this should be returned to the Kraft bag, and if necessary, the Kraft bags should be repaired or replaced and renumbered. The sample bags should be stored upright and after 4-5 hours, or at the beginning of the next day, the clear supernatant water should be carefully decanted, taking care not to pour-off the fine sediment (this process may need to be repeated for very wet samples). The samples should be left to dry in a well-ventilated place, preferably in sunlight. Samples with a high clay content need to be "massaged" from time to time to prevent caking and the formation of hard material which is difficult to disaggregate.

